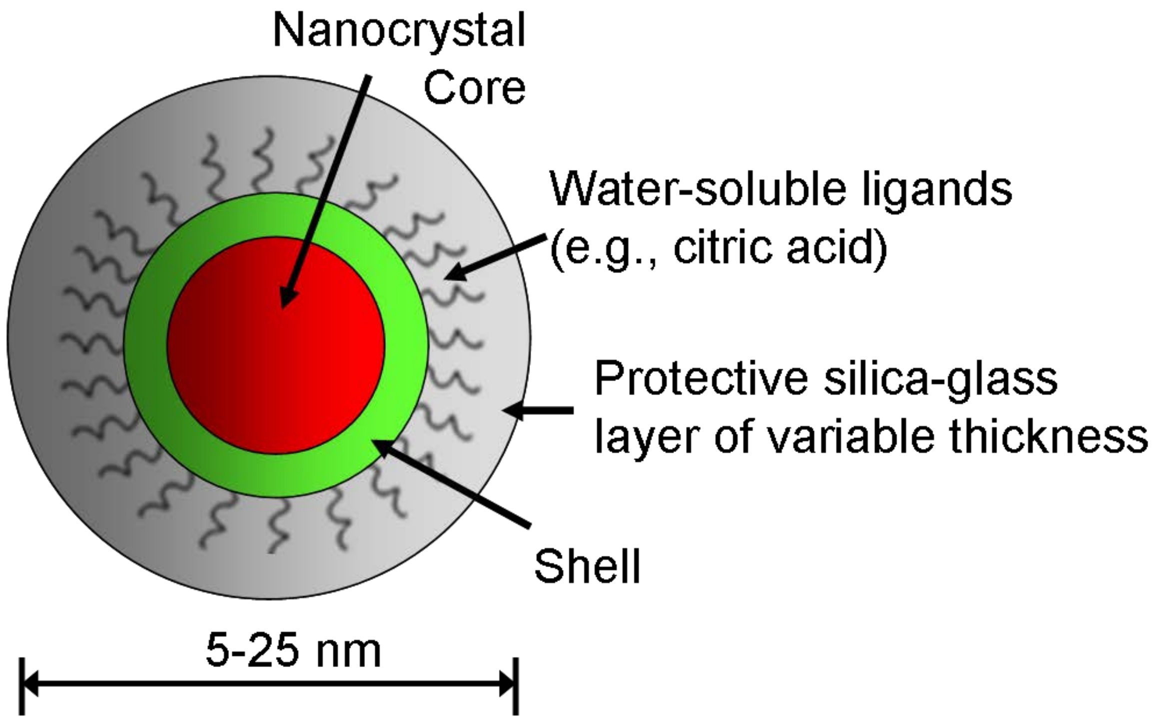

Quantum Dot Tracers for Use in Engineered Geothermal Systems DE-EE0002768

Project Officer: Lauren Boyd

Total Project Funding: $1,238,499

April 23, 2013

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***Michael Bartl*, Department of Chemistry at the University of Utah**
***Paul Reimus*, Los Alamos National Lab**

Objective

The objective of this project is to develop and demonstrate a new class of tracers, colloidal quantum dots, that offer great promise for use in characterizing fracture networks in EGS reservoirs. Since the wavelength of fluorescence (color) of these particles is a function only of diameter, they offer potentially a limitless number of individual geothermal tracers. Not only do they offer great versatility and applicability as conservative (nonreactive) tracers, but through modifications of surface properties and diameters, they can be transformed into reactive tracers that will sorb and diffuse in predictable ways and thereby be used to determine fracture surface areas.

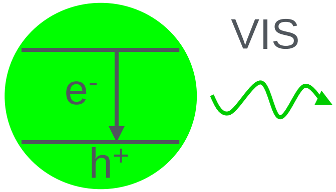
Relevance/Impact of Research

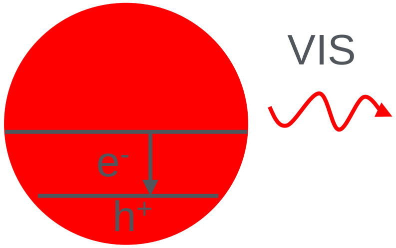
- **EGS Barriers (as identified in the 2009 EGS DOE Road Mapping Exercise) that this project is intended to overcome:**
  - Barrier J: Tracers—inadequate tracers and/or tracer methodology to accurately define the subsurface system of fractures and mapping of fluid flow
  - Limited fracture detection capability
  - Limited flow path identification capacity
  - Lack of suitable tracers
- **Innovation and Impact:**
  - For conventional geothermal and EGS applications, the number of tracers is insufficient to satisfy demand. The development and implementation of quantum dots could greatly increase the number of thermally stable and detectable tracers. Likewise, since quantum dots fluoresce at visible—and longer—wavelengths (the region of the spectrum where there are few naturally occurring interferences), the use of quantum dot tracers is conducive to automated tracing techniques. The need to take samples and send them to qualified laboratories for analysis by liquid chromatography would be eliminated, thus greatly reducing the cost and time required.
  - For EGS applications, the surface chemistry of the quantum dot tracers can be modified to allow them to sorb and desorb in a predictable manner. In combination with numerical modeling, this property can serve to measure the surface area for sorption, which is related to the surface area for heat extraction.

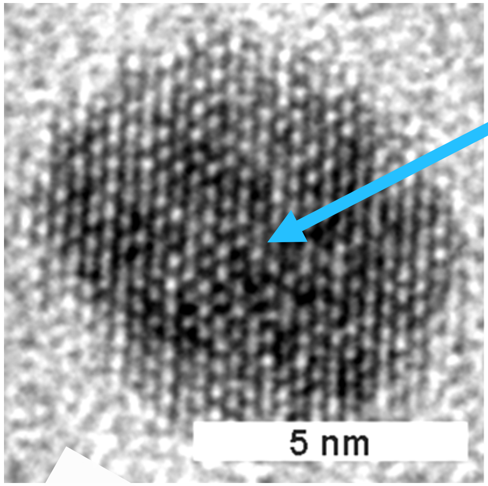
Scientific/Technical Approach

Quantum Size Effect

Electronic and optical properties of semiconductor nanocrystals can be continuously tuned in the visible and near-infrared regions by "adjusting" their size:

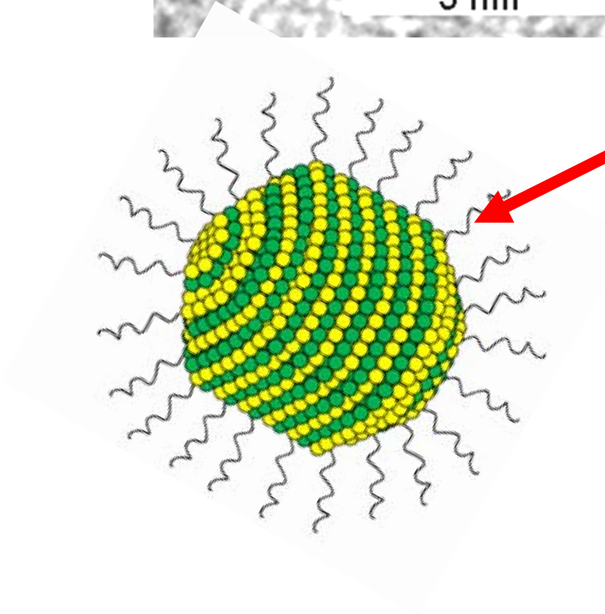






Physics

Optical Properties



Chemistry

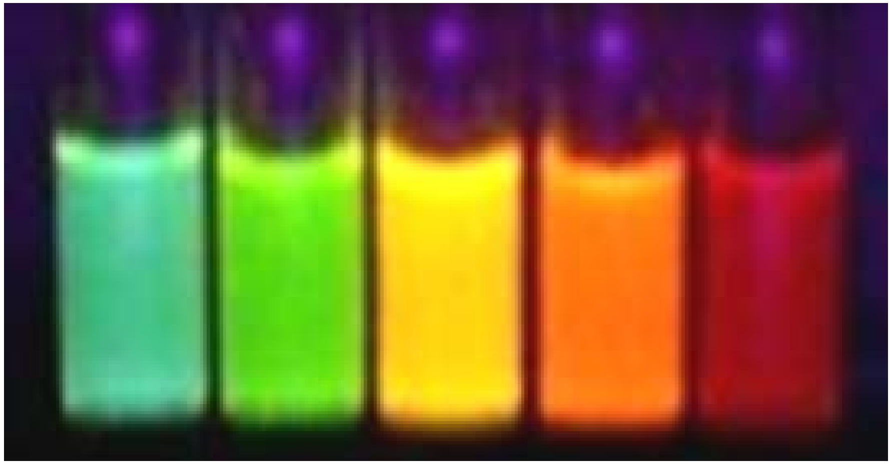
Hydrophobic–Hydrophilic Surfactants

- specific functionalities (amines, carboxylates, acrylates etc.)
- surface charge (positive/negative groups)

Summary of Scientific/Technical Approach

- *Synthesize laboratory quantities of nonsorptive quantum-dot tracers that fluoresce in the visible*
- *Test the quantum dot tracers for thermal stability and detectability*
- *Test the nonsorptive quantum dot tracers in benchtop reactors*
- *Modify the surface chemistry of the quantum dots to allow for interaction with fracture surfaces:*
  - *Reversible sorption on negatively charged rocks*
  - *Thermal decay*
  - *Contrasting diffusivity into vein pores*
- *Develop analytical/numerical models for the interaction of the quantum dot tracers with reservoir rock*
- *Synthesize kilogram quantities of quantum-dot tracers for use in field tests*
- *Field test the quantum dot tracers (nonsorptive, sorptive, diffusive and thermally decaying) in single-well injection/backflow applications*

Accomplishments, Results and Progress



OUR METHOD

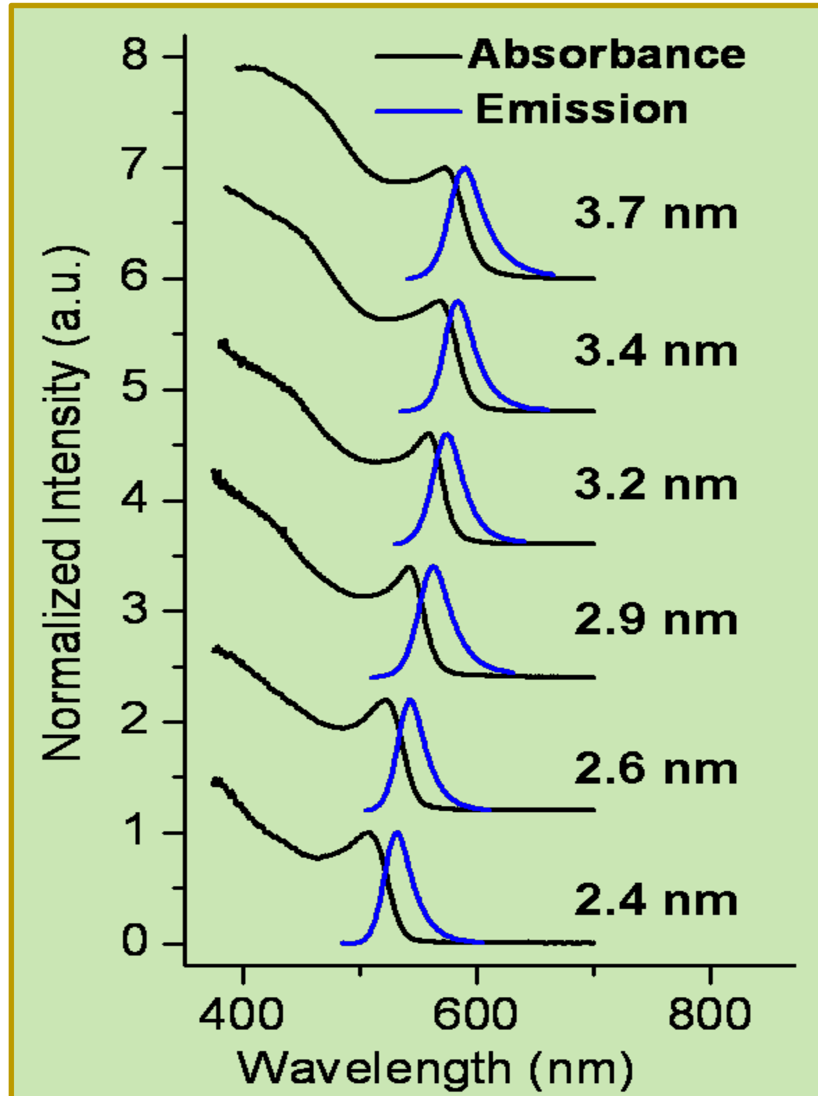
low temperatures 50-130 ºC

modest precursor injection

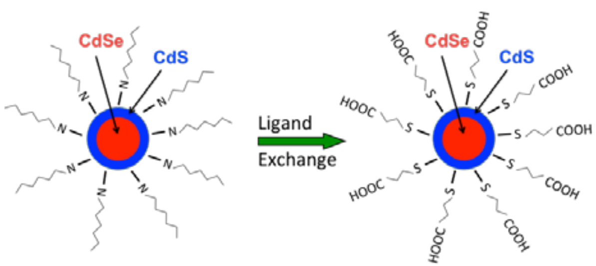
slow decomposition

crystal nucleation and **growth**

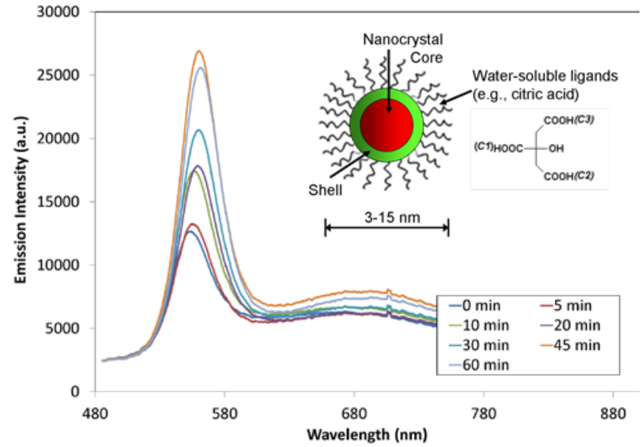
Bartl, M.H. & Siy, J.T. *Patent Application* **61/145,477** and *Patent Application* **61/145,925**.



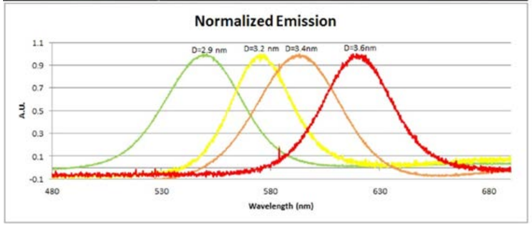
Synthesis of core/shell/ligand quantum dot tracers using newly developed Bartl low-temperature methods:



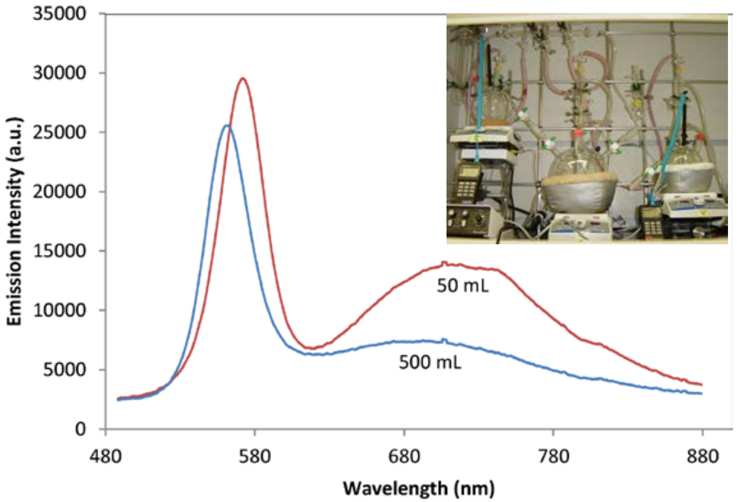
A ligand exchange following the low temperature synthesis renders the quantum dot tracers water soluble.



Optimization of the ratios of the cadmium and selenium as well as the timing for the addition of sulfur allows for optimum yields.

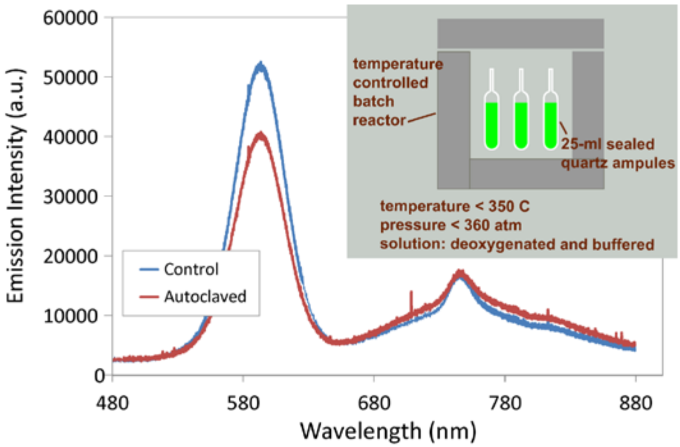


Further optimization of temperature, pH, and concentrations allows for the range in size that controls emission wavelength.

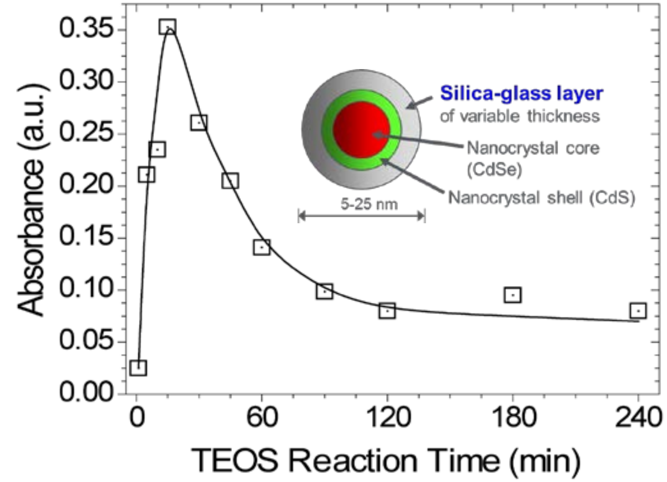


Finally, upscaling resulted in a 1,000-fold increase in yield, while improving quantum dot quality.

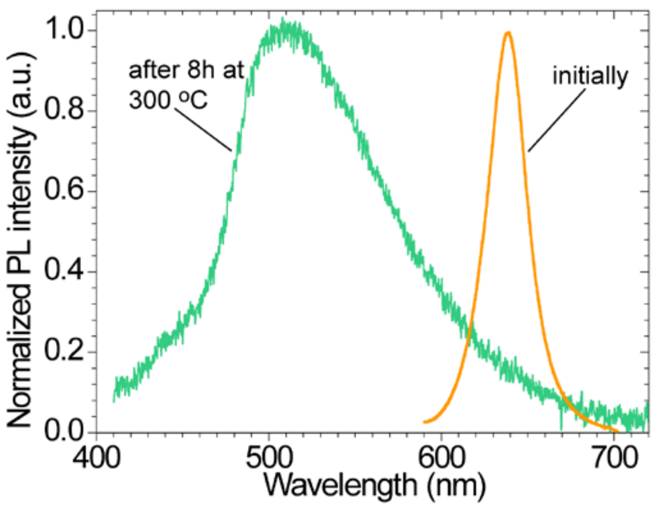
Silica encapsulation to enhance thermal stability:



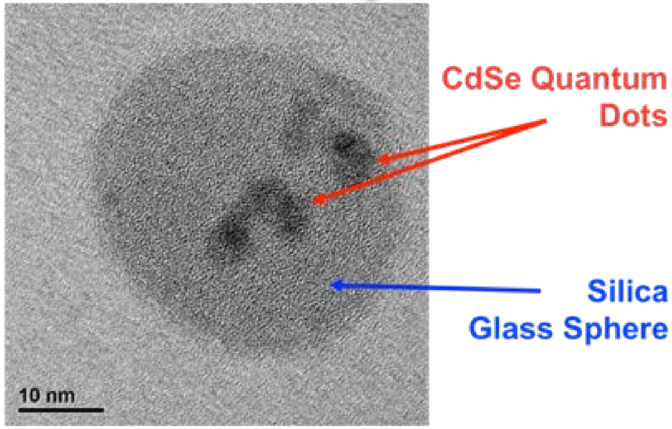
Slight decrease in emission intensity for CdSe/CdS quantum dots after exposure to simulated geothermal conditions for 4 h at 150ºC. Better thermal stability needed.



Method optimized for encapsu-lating the CdSe/CdS quantum dot in a protective silica-glass shell.



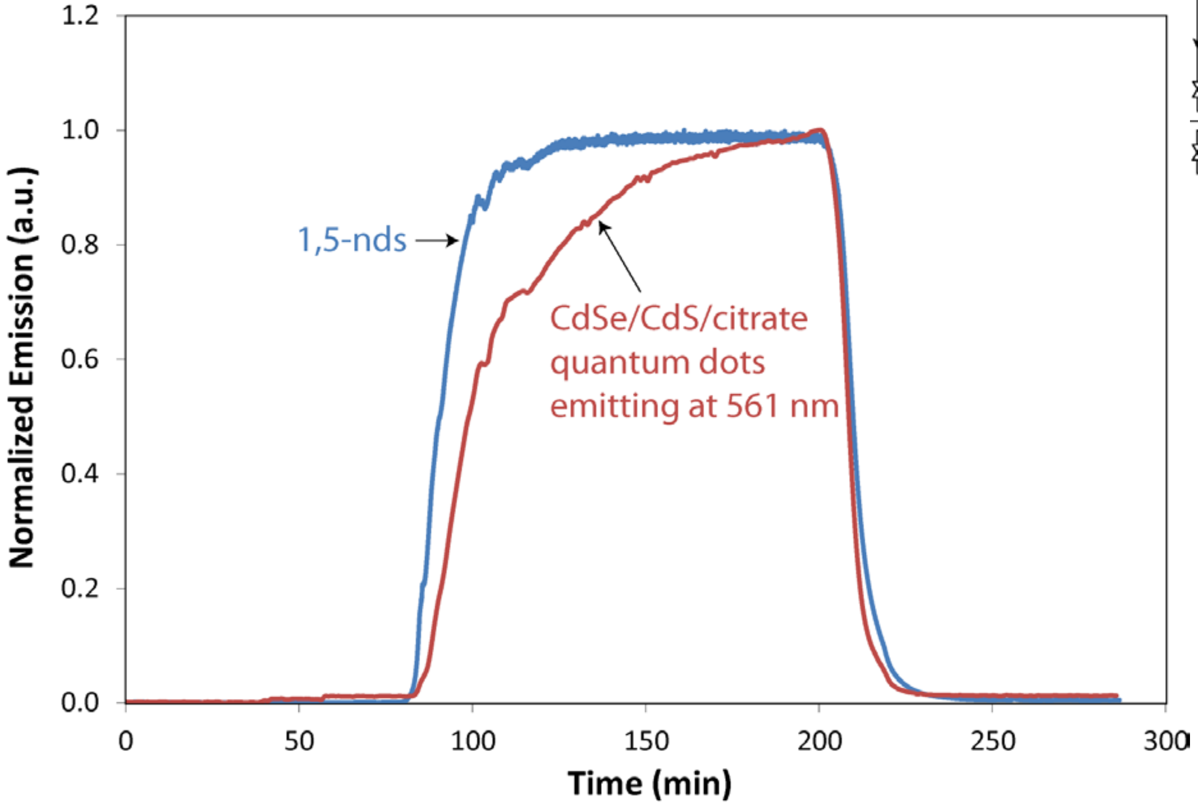
Increase in luminescence of CdSe/ZnS/SiO_2 quantum dots by a factor of 3.5 after eight hours at 300ºC. But the concomitant blue shift shows oxidation and shrinkage of the inner CdSe core.

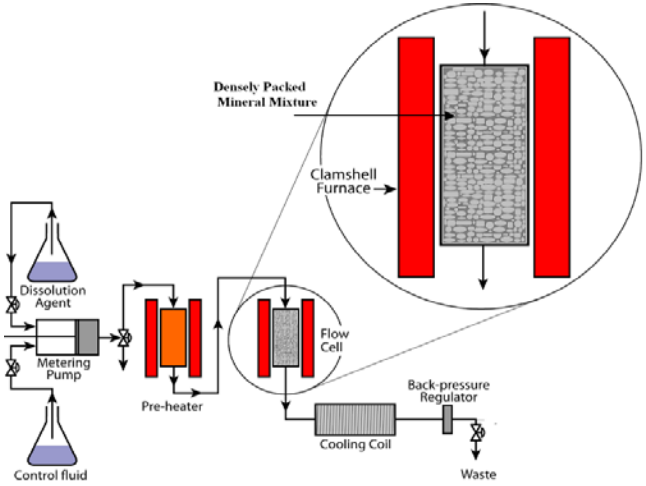


Lumines-cence enhance-ment of silica-coated quantum dots with increased loading.

Riassetto, Ma, Amador, Benson, Briggs, Mella, Rose, Bartl, (2011)"Biphasic Route to Silica-Encapsulation of Quantum Dots", Nanosci. Nanotechnol. Lett., **3**, pp. 655-658.

Flow of CdSe/CdS/citrate quantum dots and a conservative solute tracer through a porous medium:





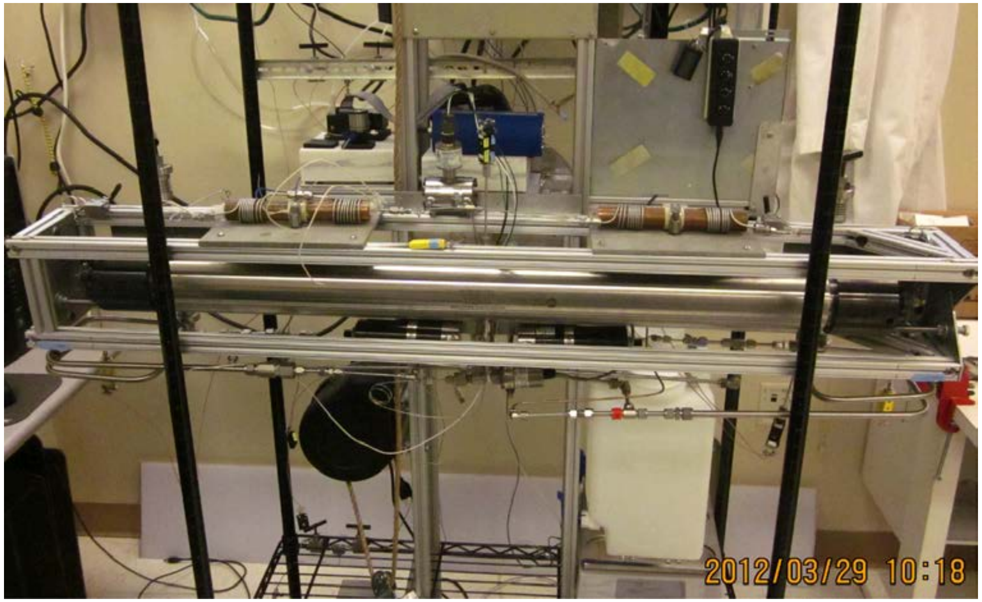
Schematic of the flow reactor

Experimental Conditions:

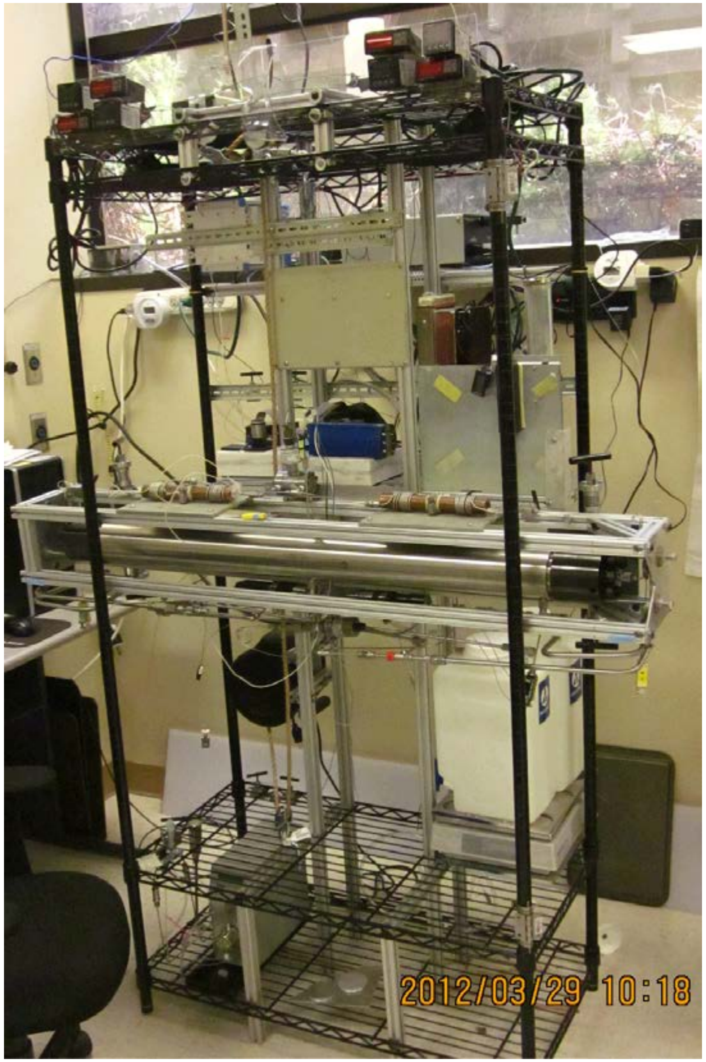
- **Column packed with Ottawa sand having 450-500 um grain size**
- **Yellowish-green CdSe/CdS/citrate quantum dots (~2.6 nm diameter)**
- **1,5-naphthalene disulfonate as the companion conservative tracer**
- **25°C column temperature**

Brauser, E., Bartl, M., and Rose, P.E. (2013) Thermal Stability and Chemistry of Fluorescent Nanocrystals for Use as a Novel Geothermal Tracer, *Proceedings, 38th Workshop on Geothermal Reservoir Engineering*, Stanford University SGP-TR-198.

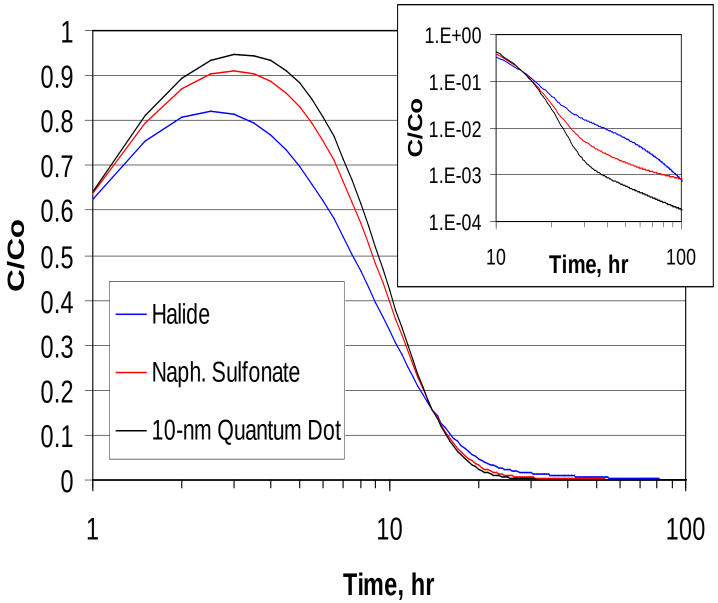
Design and Fabrication of a Flow Reactor for Testing the Performance of Quantum Dot Tracers under Single-Well Injection-Withdrawal Conditions

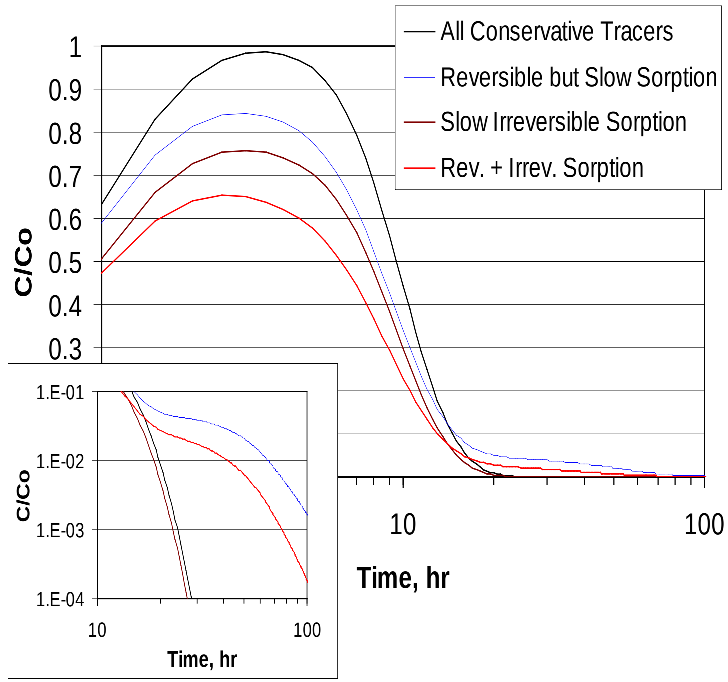


Maximum Temperature	425°C (800°F)
Maximum Pressure	290 bar (4,250 psi)
Column Dimensions	40" x 2" (102 cm x 5 cm)
Column Volume	0.5 gal (2 liter)
Surface area when filled with coarse sand	964 m^2



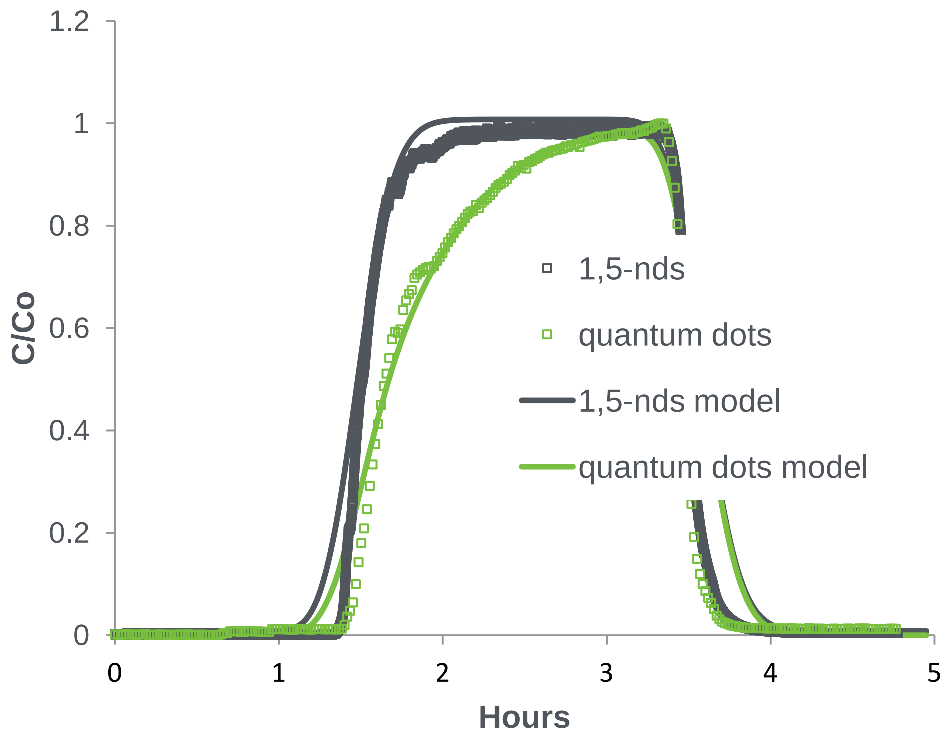
Development of Single-Well Injection-Withdrawal (SWIW) Model Showing Quantum Dot Tracers as either Conservative or Reactive





MULTRAN simulations of single-well injection-withdrawal tracer tests in which a quantum dot tracer is nonsorbing and thus serving as a conservative tracer with a much smaller diffusion coefficient than a solute tracer (above left). The figure on the right shows a quantum dot (or other tracer) sorbing reversibly and thus serving as the reactive tracer.

Flow Modeling of Quantum Dot Tracers



Simulations of experiments of the solute tracer, 1,5-naphthalene disulfonate, ands the 2.6-nm yellowish quantum dots (CdSe/CdS/citrate) flowing through a sand-packed column at 25^{o}C. The semi-analytical code RELAP captures reasonably well the behavior of both the solute and colloidal tracers.

Future Directions

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Remaining challenges during this grant:

- Solve the long-term stability problem (under both ambient and high temperature geothermal conditions) for conservative quantum dot tracers by developing improved ligand chemistry.
- Develop ligand chemistry that will allow for the rapid sorption and desorption of ‘reactive’ quantum dot tracers.
- Conduct injection-backflow experiments using the SWIW reactor to confirm the performance of the sorbing/diffusing quantum dot tracers relative to that of a conservative solute tracer.

Primary challenges for follow-on grant:

- Design, synthesize, and characterize quantum dot tracers using environmentally acceptable metals (e.g. Zn, Cu, Mg, Fe, Mn).
- Develop and demonstrate suitable surface chemistry that will allow for long term stability both and room and geothermal temperatures.
- Scale up synthesis to provide kg quantities.
- Demonstrate the use of quantum dot tracers in geothermal fields.

Mandatory Summary Slide

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

	FY2010	FY2011	FY2012	FY2013
Target/Milestone: Development of methods for the synthesis of quantum dot tracers	1. Develop a method for the synthesis of hydrophobic quantum dot tracers, followed by ligand exchange to render them hydrophilic. 2. Modify the above approach for the direct synthesis of hydrophilic quantum dots. 3. Develop first silica encapsulation of quantum dot tracers.	1. Test the performance of the proxy quantum dot tracers in a flow reactor 2. Develop initial numerical model for inverting quantum dot tracer data for surface area determination from SWIW tests 3. Synthesize large diameter (2nd gen) quantum dots. 4. Determine thermal stability of quantum dot tracers. 5. Investigate improved synthesis of silica shells 6. Design and fabricate SWIW reactor.	1. Test the performance of the proxy quantum dot tracers in a flow reactor. 2. Fabricate SWIW reactor	1. Test the performance of real quantum dot tracers in a flow reactor. 2. Develop synthesis and purification techniques (including the use of a citrate and PEG ligands) to improve long term stability.
Results	1. Task completed Q1 2. Task completed Q3 3. Task completed Q4 Results presented October, 2010, at the annual meeting of the Geothermal Resources Council, Sacramento, CA.	1. Task initiated Q4. 2. Task completed Q4. 3. Task completed Q2. 4. Task completed Q1. 5. Task completed Q4, but results showed unwanted clustering over long periods. 6. Design complete but fabrication continues. Results presented at Stanford Geothermal Workshop, Feb., 2011; AAPG, March 2011;	1. Task completed Q1. 2. Task completed Q2. Results presented at AGU, Dec. 2011; Stanford Geothermal Workshop, Feb., 2012	1. Task completed Q1. 2. Progress made but work continues. Results presented at Stanford Geothermal Workshop, Feb., 2013

Project Management

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Timeline:

Planned Start Date	Planned End Date	Actual Start Date	Current End Date
10/01/2009	9/30/2012	01/29/2010	9/30/2013

Budget:

Federal Share	Cost Share	Planned Expenses to Date	Actual Expenses to Date	Value of Work Completed to Date	Funding Needed to Complete Work
$768,059	$470,439	$1,238,498	$1,200,000	$1,200,000	$38,498

- Summary of project management achievements:
  - This project was a successful collaboration between chemical synthesis (by the Bartl group in the Department of Chemistry at the U of Utah), testing under simulated geothermal conditions (by the Rose group at EGI), and flow modeling (by Paul Reimus at LANL).
  - The project was conducted in parallel to another tracer project at EGI (“Tracer Methods for Characterizing Fracture Creation in Engineered Geothermal Systems”), which had as an objective the creation of “smart” (primarily sorbing) tracers for characterizing the fracture surface area of newly created fractures. Concepts developed in the creation of reactive geothermal solute tracers were directly relevant to the development of laboratory testing methods for characterizing the quantum dot tracers.